

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : WO 96/19281
B01D 53/75, C01B 17/16, 17/98 (11) International Publication Number:
A1 (43) International Publication Date: 27 June 1996 (27.06.96)

(21) International Application Number: PCT/US95/15964

(11) International Publication Number: WO 96/19281

(22) International Filing Date: 12 December 1995 (12.12.95)

(43) International Publication Date: 27 June 1996 (27.06.96)

(30) Priority Data: 08/358,916 19 December 1994 (19.12.94) US

(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(71) Applicant: FLUOR CORPORATION [US/US]; 3333 Michelson Drive, Irvine, CA 92730 (US).

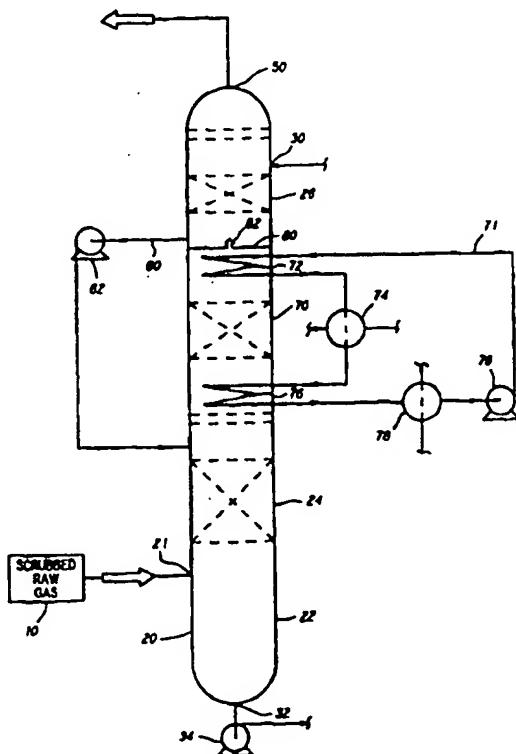
(72) Inventors: MORTON, Thomas, E.; 3151 Fairview Drive, Vista, CA 92084 (US). RAO, Ashok, D.; 50 Seqada, Rancho Santa Margarita, CA 92688 (US).

(74) Agent: FISH, Robert, D.; 3000 South Augusta Court, La Habra, CA 90631 (US).

(54) Title: INTEGRATED COS-H₂S HYDROLYSIS PROCESS

(57) Abstract

Gas streams (10) containing substantial concentrations of COS and H₂S contaminants are cleansed by removing the bulk of the H₂S in a first absorber (20), reacting the COS to form H₂S in a hydrolysis unit (44), and then removing most or all of the remaining H₂S using a second absorber (22). This reduces the total sulfur contained in the stream and/or reduce the number of trays required in the absorbers (20) and (22).



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

S P E C I F I C A T I O N

INTEGRATED COS-H₂S HYDROLYSIS PROCESS

5

BACKGROUND OF THE INVENTION

The present invention relates to the field of gas and hydrocarbon processing.

10 Modern gas and hydrocarbon processing plants often produce products in which carbonyl sulfide (COS) and/or hydrogen sulfide (H₂S) are present as pollutants. Such processes include gasification combined cycle and synthesis gas plants utilizing coal, coke, oil or emulsion, and 15 refineries using thermoconversion processes such as visbreaking, thermal cracking or coking. Due to environmental and other restrictions it may be desirable to minimize these pollutants in the final emissions.

20 In the existing art with most acid gas removal processes, (AGR), the depth of sulfur removal is constrained by the amount of COS present in the feed gas. Where there are significant concentrations of COS in the feed gas, the current practice is to hydrolyze the COS to H₂S before the absorber 25 that removes the H₂S. In that practice, the hydrolysis reaction is stopped when the partial pressure of H₂S reaches

- 2 -

equilibrium, and a relatively high level of COS remains in the emissions. The problem is exacerbated when there is already a large concentration of H₂S present in the feed gas, and where the COS has a lower reactivity with the absorbing solvent of 5 the AGR. In some circumstances, higher concentrations of COS may require more absorber trays to remove the COS than are used to remove the H₂S. In general, prior art removal of COS by absorption is usually limited to approximately 50% of that present in the feed gas.

10

The current practice for producing very low sulfur synthesis gas is to use the Rectisol process. This process can achieve removal of the H₂S and the COS almost completely by operating at very low temperatures. The process is complex 15 and both capital and energy intensive because of the high refrigeration requirements. No other commercial process is known to remove COS to low levels solely by absorption. The process also removes most of the CO₂, which is a disadvantage where the synthesis gas is to be used as turbine fuel because 20 of the subsequent decreased power output.

Although other acid gas removal (AGR) systems have little ability to remove COS, many of them can achieve significant CO₂ slip in combination with sulfur levels below 50 ppmv much more

- 3 -

economically than the Rectisol process through a combination of two process operations:

1. Shifting the COS to H₂S in a COS hydrolysis reactor upstream of the AGR unit. The ability to do this is limited by the equilibrium constant and the large amount of H₂S in the gas.
2. Using high solution circulation rates and cooling of the solution until limited by high solution viscosities to achieve the maximum amount of H₂S and residual COS removal. This combination of operating conditions is not consistent with achieving maximum CO₂ slip.

Further removal of sulfur in this manner requires the consumption of a chemical such as zinc oxide, requiring additional equipment, chemicals cost and disposal changes.

Accordingly, it is an object of the invention to provide an improved means of removing sulfur compounds from a feed gas. Other and further objects and advantages will appear hereinafter.

SUMMARY OF THE INVENTION

To these ends, the partial pressure of H₂S in a feed gas is reduced prior to COS removal. The gas is then fed into a

- 4 -

COS hydrolysis reactor where the COS is hydrolyzed to H₂S. Due to the significantly lower H₂S partial pressure in the stream fed into the COS hydrolysis reactor, as compared to the H₂S partial pressure in the feed gas, essentially all of the COS 5 is converted to H₂S. The reactor effluent is then further treated to remove additional H₂S.

BRIEF DESCRIPTION OF THE DRAWING

In the drawings, wherein similar reference characters 10 denote similar elements throughout the several views:

Figure 1 is a schematic of a prior art COS removal system.

Figure 2 is a schematic of a COS removal system where the COS reactor is external to the H₂S absorber tower.

15 Figure 3 is a schematic of a COS removal system where the COS reactor is internal to the H₂S absorber tower.

DETAILED DESCRIPTION OF THE DRAWINGS

The prior art system of Figure 1 is characterized by the 20 fact that COS in a gas stream is hydrolyzed to H₂S prior to removal of H₂S. Considering the process in greater detail, scrubbed raw gas 10 is cooled in cold water cooling unit 110, and then enters a COS hydrolysis reactor 120 in which a portion of the COS is transformed into H₂S. The gas then is 25 passed through a low temperature gas cooling unit 130, and

- 5 -

enters an H₂S absorber tower 140 at point 142. The gas flows through absorber tower 140 countercurrently to a physical or chemical solvent 150, and exits the top of tower 140 at point 144. Solvent 150 enters tower 140 at point 152, and exits 5 absorbent tower 140 at point 154.

In Figure 2, H₂S is removed from a gas stream both prior to and following hydrolysis of COS, not merely following hydrolysis. In this embodiment scrubbed raw gas 10 is fed 10 along line 11 into a low temperature gas cooling unit 12, and thereafter into an H₂S absorber tower 20 along line 13. The absorber tower 20 comprises a lower section 22, a middle section 24, and an upper section 26. A solvent 30 which absorbs H₂S enters the tower 20 at point 31, and exits the 15 tower 20 at point 32. Appropriate solvents 30 may be of the same composition as solvent 150 in Figure 1, and are well known in the art. The upper portion 26 of absorber 20 is separated from the middle portion 24 of absorber 20 by divider 26. The solvent passes between the upper portion 26 and the 20 middle portion 24 through path 60 under the influence of pump 62.

Upon entering tower 20, the raw gas 10 proceeds up the tower countercurrently to solvent 30, and exits tower 20 at 25 point 40. After heat exchange in heat exchange unit 42, the

- 6 -

gas proceeds to a COS hydrolysis reactor 44 along line 43, in which COS contained within the gas is at least partially hydrolyzed to H₂S according to the following reaction:



5 Following hydrolysis in reactor 44, the gas stream exits the reactor along line 45 and is cooled with cold water in cooling unit 46, and reintroduced into absorber tower 22 at point 48. The gas is once again run countercurrently to solvent 30 within absorber 22 to remove H₂S, and then finally exits 10 absorber 22 at point 50 along line 51.

In Figure 3 H₂S is also removed from a gas stream both prior to and following hydrolysis of COS, however, the COS hydrolysis reactor is contained within the H₂S absorber. In 15 this embodiment scrubbed raw gas 10 is introduced into H₂S absorber tower 20 at point 21. Absorber tower 20 has multiple stages, including a lower portion 22, a first H₂S absorber section 24, a COS hydrolysis catalyst bed 70, and an upper or second H₂S absorber section 26. As in Figure 1, lean solvent 20 is introduced into absorber tower 20 at point 30, and exits absorber tower 20 at point 32. In Figure 3, the "used" or "rich" solvent is pumped from the bottom of absorber tower 20 by pump 34. There is a barrier 80 within absorber tower 20 between the catalyst bed 70 and the second absorber section 25 26. Barrier 80 contains an opening 82 through which the gas

- 7 -

can flow up the tower. The solvent bypasses barrier 80 by flowing through line 60 under the influence of pump 62. To increase the temperature of gas 10 to the reaction temperature as required by the COS hydrolysis catalyst contained in bed 5 70, a separate heat transfer system is provided. In this system, a relatively cool fluid flows through the line 71 to cool gas at heat exchanger 72. The heated fluid then is further heated at heat exchanger 76, and re-enters absorber tower 20 where it heats gas 10 in heat exchanger 76 to the 10 reaction temperature. The fluid is then cooled in cooling unit 78. The fluid is pumped through half way 71 under the influence of pump 79.

As apparent from the above descriptions, the main 15 difference in the embodiments of Figures 2 and 3 is the positioning of the hydrolysis reactor. In Figure 2, the hydrolysis reactor 34 is external to the absorber tower 20. In Figure 3, the COS hydrolysis catalyst bed is internal to and integral with the absorber tower 20. The embodiment of 20 Figure 2 is advantageous because the equipment configuration does not require any development. The embodiment of Figure 3 is particularly advantageous because a separate reaction vessel is not required.

The processes shown in Figures 2 and 3 are capable of reducing the total sulfur emissions contained in a feed gas stream, and in particular of reducing the COS concentration of such a stream to less than 2 ppmV. This achievement is 5 largely due to the fact that the partial pressure of H₂S in the gas stream entering reactor 44 is significantly lower than that found in the raw gas 10, essentially all the COS in the stream having been converted to H₂S. This is evidenced by the calculated values from actual equilibrium data, as presented 10 in Table 1 below.

Table 1

	STREAM NO. COMPOUND	13. AGR FEED	43. COS HYD FEED	45. COS HYD EFFL.	51. AGR EFFL.
15	H ₂	10,731.20	10,728.40	10,728.40	10,728.40
	N ₂	279.70	279.40	279.40	279.40
	CO	15,590.10	15,586.80	15,586.80	15,586.80
	CO ₂	3,432.80	3,127.20	3,133.17	3,133.17
20	H ₂ S	299.20	0.30	6.27	0.30
	COS	7.50	6.00	0.03	0.03
	C ₁	56.80	56.80	56.80	56.80
	H ₂ O	88.17	88.17	82.20	82.20
	AR	346.00	346.00	346.00	346.00
25	-----				

TOTAL MOLS	30,831.17	30,219.08	30,219.08	30,213.11
TOTAL LBS#	644,184.94	620,362.00	620,362.00	620,158.44
TEMP 'F	103.00	300.00	300.29	115.00
PSIA	375.00	370.00	360.00	355.00
5 MM-BTU/HR	3,317.53	3,287.86	3,287.86	3,245.30
WATER-MPH	0.00	0.00	0.00	0.00

While the methods and systems described herein can be used with gas streams containing little COS or H₂S, they are 10 most useful with streams having substantial concentrations of H₂S. The term substantial concentration of H₂S as used herein refers to streams having H₂S concentration of at least 10 ppmV, and substantial concentration of COS refers to streams having COS concentration of at least 10 ppmV.

15 In processes such as Selexol that absorb COS, the benefits from the methods and systems described herein may be realized in the form of reduced solvent circulation rate and thus reduced utility consumptions as well as reduced equipment 20 costs.

The integrated COS hydrolysis/acid gas removal process can achieve low sulfur synthesis gas in any of the more economical AGR systems by eliminating the equilibrium 25 restraints on the COS hydrolysis unit, as explained

- 10 -

previously. CO₂ slippage can also be maximized with this configuration.

The various components identified in Figures 1, 2 and 3
5 all fall well within the knowledge of those having ordinary
skill in the art. For example, the H₂S absorber may be packed
column, a tray column or any other gas/liquid contact device
such as a HiGee® unit or a venturi scrubber. Appropriate
hydrolysis reactors include fixed beds, moving beds, fluidized
10 beds and entrained beds.

There are numerous alternative embodiments of the claimed
invention to that shown in Figures 2 and 3. For example, COS
reactor 44 could be positioned partly within and partly
15 without absorber tower 20, and two or more hydrolysis reactors
may be utilized in place of the single reactor. Similarly,
absorber tower 20 is depicted as a single unit having multiple
sections, but may be embodied as two or more physically
separate absorbers. The heating and cooling units may also be
20 repositioned, or increased or decreased in number, according
to the temperature and pressure of the gas stream within the
system.

Thus, a method and system for removing COS from a feed
25 gas stream has been disclosed. While specific embodiments and

- 11 -

applications of this invention have been shown and described, it would be apparent to those skilled in the art that many more modifications are possible without departing from the inventive concepts herein. The invention, therefore, is not to be restricted except in the spirit of the appended claims.

5

- 12 -

What is claimed is:

1. A method for removing COS from a gas stream containing H₂S, comprising the steps of:
 - removing H₂S from the gas stream;
 - 5 thereafter converting at least some of the COS in the stream to H₂S; and
 - then removing additional H₂S from the stream.
- 10 2. The method of claim 1 wherein removal of H₂S comprises contacting the stream gas with at least one of a physical and chemical solvents.
- 15 3. The method of claim 2 wherein removal of H₂S and conversion of COS to H₂S occur within a single tower.
4. The method of claim 2 wherein conversion of COS to H₂S occurs in a unit external to that employed to remove H₂S.
- 20 5. A method of removing COS from a feed gas stream containing a substantial concentration of H₂S, comprising the sequential steps of:
 - providing an absorber unit containing a solvent capable of removing H₂S, the solvent flowing from an upstream portion within the absorber unit to a downstream portion within the absorber unit;

- 13 -

countercurrently contacting the solvent within the downstream portion with the gas stream such that H₂S is removed from the gas stream;

5 removing at least a portion of the gas stream from contact with the solvent;

hydrolyzing COS in the gas stream to H₂S;

countercurrently contacting the solvent within the upstream portion with the gas stream; and

removing the gas stream from the absorber unit.

10

6. A gas cleaning system comprising:

first and second H₂S absorber units;

a COS hydrolysis unit; and

15 a pathway conducting the gas sequentially from the first absorber unit to the hydrolysis unit to the second absorber unit.

20 7. The system of claim 6 wherein the hydrolysis unit and at least one of the absorber units are contained within a single tower.

8. The system of claim 6 wherein the hydrolysis unit and the first and second absorber units are contained within a single tower.

25

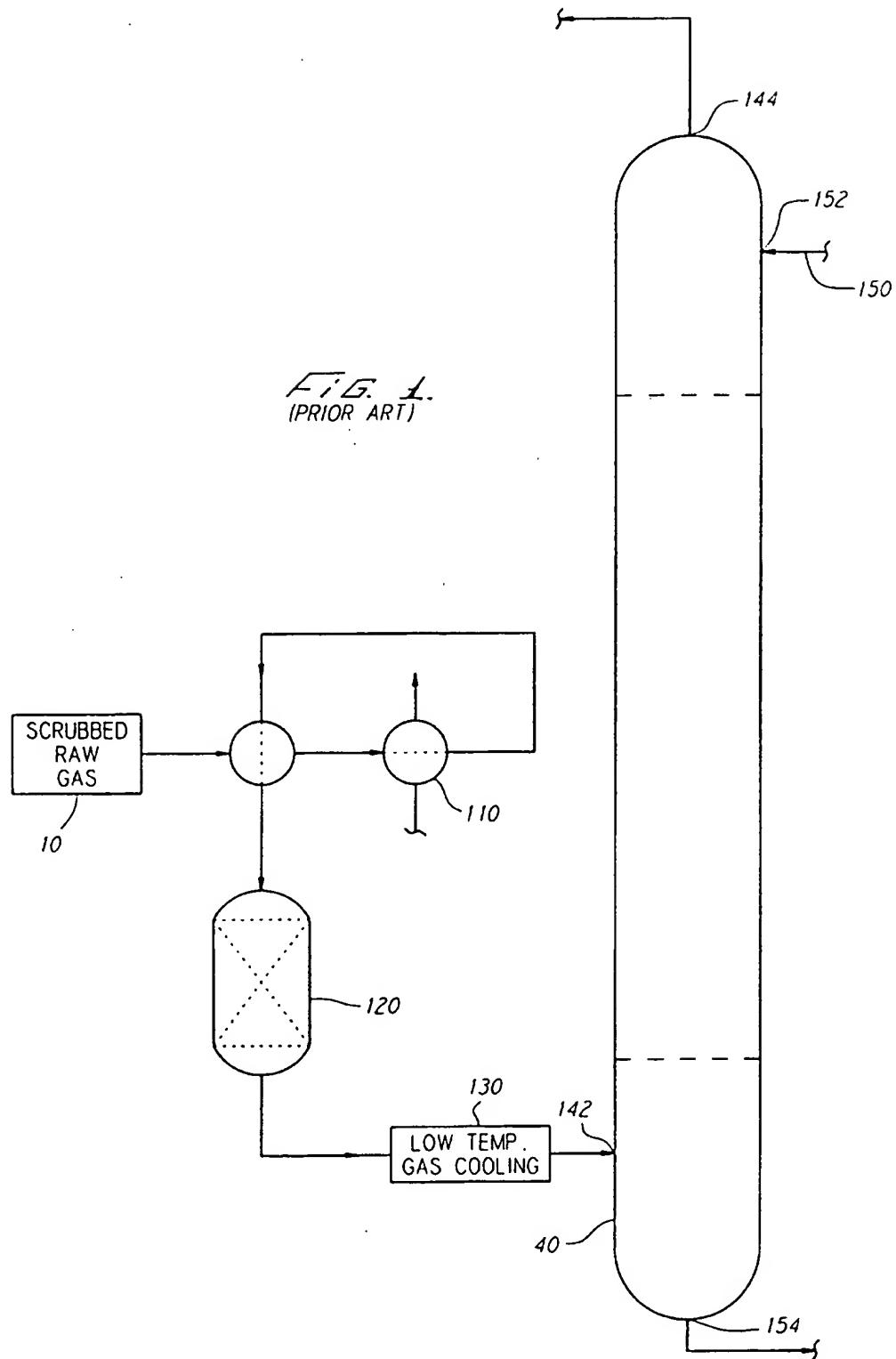
- 14 -

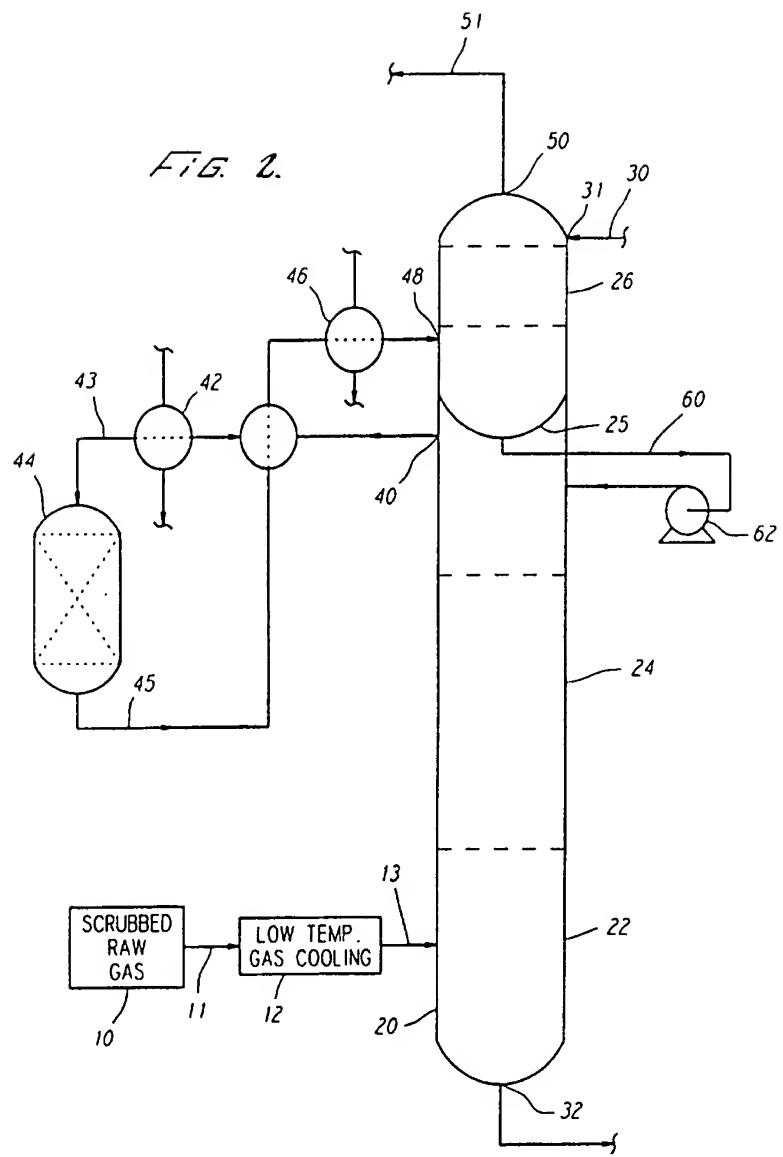
9. The system of claims 7 or 8 wherein at least one of the absorber units contains a solvent which flows countercurrently relative to the gas.

5 10. The system of claim 9 wherein the solvent comprises at least one of a physical and chemical solvent.

11. In a system for removing sulfur compounds from a gas stream, said system having an H₂S absorber and a COS hydrolysis 10 reactor, an improvement comprising a flow path which carries the gas through portions of the absorber both prior to and following treatment of the gas by the reactor.

12. The improved system of claim 11 wherein the reactor 15 is contained within the tower.





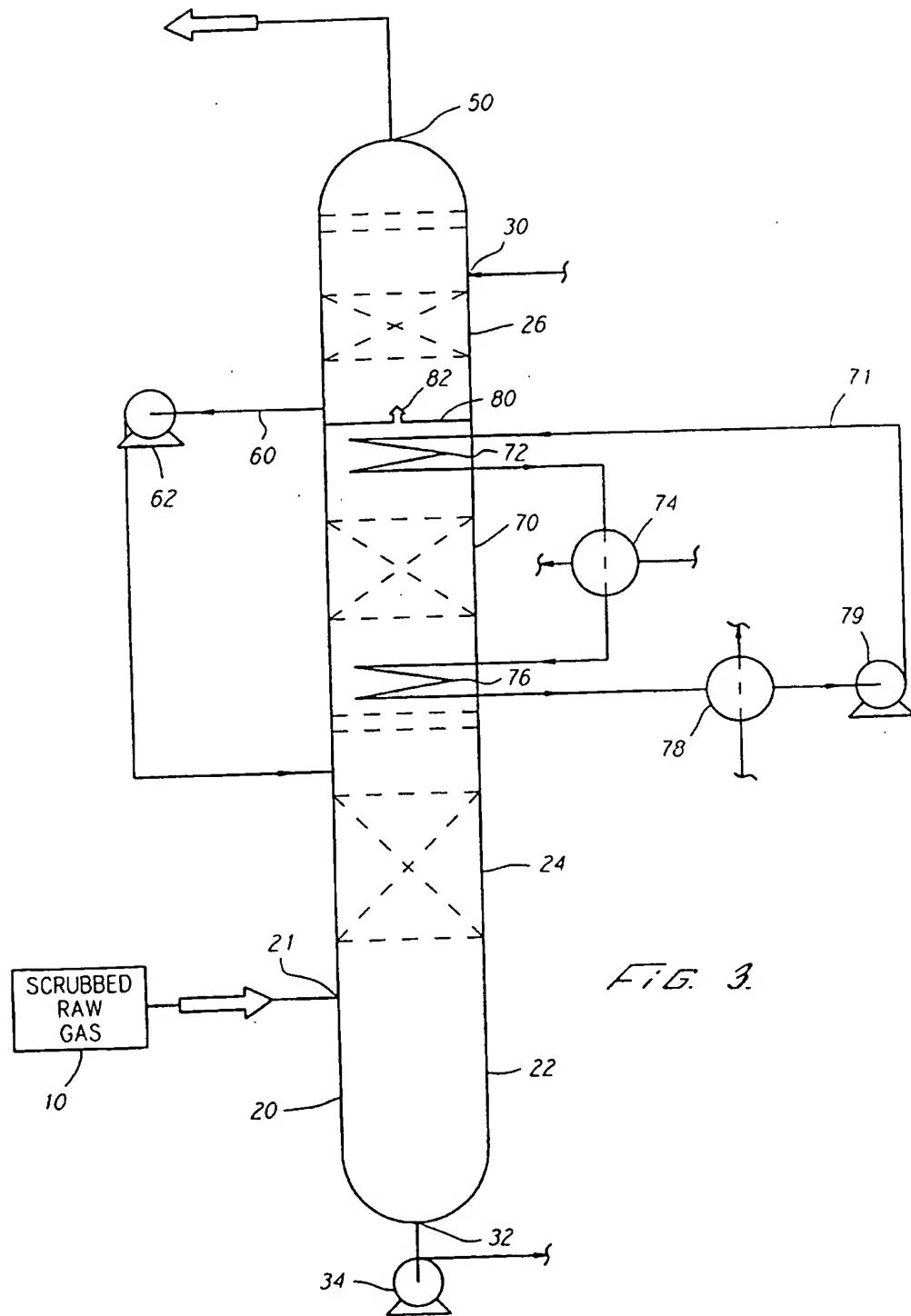


FIG. 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15964

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B01D 53/75; C01B 17/16, 17/98

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/226, 242.1, 563, 576.2, 576.6, 655; 95/161, 163, 166, 235; 422/169, 171

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,254,094 (HEGARTY) 03 March 1981, col. 3, lines 29-61; col. 4, lines 38--49.	1-2, 4, 6, 9-11
X	US, A, 4,409,199 (BLYTAS) 11 October 1983, col. 8, lines 30-68; col. 9, lines 1-4.	1-2, 4, 6, 9-11
X	US, A, 4,332,781 (LIEDER ET AL.) 01 June 1982, col. 6, lines 13-50.	1-2, 4, 6, 9-11
Y	US, A, 3,965,244 (SYKES, JR.) 22 June 1976, col. 8, lines 51-68; col. 9, lines 1-50.	3, 5, 7-8, 12

 Further documents are listed in the continuation of Box C. See patent family annex.

•	Special categories of cited documents:	
'A'	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
'E'	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
'L'	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
'O'	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
'P'	document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 March 1996

Date of mailing of the international search report

18 APR 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer
DAVID A. SIMMONS

Telephone No. (703) 308-1972